

Infrared study of adsorption of acetophenones on silica–alumina

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Abstract

Infrared spectra are reported of acetophenone and 4-methoxyacetophenone adsorbed on silica–alumina catalyst. The dominant modes of adsorption involved ligation via carbonyl groups to Lewis acidic Al^{3+} sites and H-bonding of surface silanol groups to carbonyl groups or aromatic rings. Isotopic H/D exchange between SiOH groups and CD_3 groups or SiOD and CH_3 occurred for acetophenone probably via an enolisation mechanism, although no enolic species could be detected. There was also little evidence for condensation reactions. Band positions for adsorbed acetophenones compared with the predictions of Hartree–Fock calculations suggested that acetophenone was not protonated, but 4-methoxyacetophenone was protonated by Brønsted acidic hydroxy groups for which $-6.15 \leq H_0 \leq -4.81$. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Acetophenones; Infrared spectra; Silica–alumina catalyst; Brønsted sites

1. Introduction

Infrared spectra of adsorbed ammonia [1] and pyridine [2,3] have been widely used to detect Lewis and Brønsted acidic sites on silica–aluminas. The IR method distinguishes between Lewis and Brønsted acidic sites [4], and enables surface concentrations of sites to be deduced providing appropriate band extinction coefficients are known [2]. Correlations with catalytic activities may then be achieved. For example, intensities of an infrared band due to pyridinium ions on a series of silica–aluminas with a range of alumina contents were linearly related to the catalytic activities of the silica–aluminas for *o*-xylene isomerisation [3]. However, pyridine

adsorption fails to distinguish sites of different Brønsted acidic strengths except in so far as with $pK_{BH}^+ = 5.2$ [5] it will only be protonated if the formal acidity function [6] assessment of site strength is $H_0 < ca. 5.2$.

One approach to characterising Brønsted sites of differing acid strengths has been to record electronic spectra (or simply observe colour changes) of adsorbed bases that have been used for the determination of acidity functions for aqueous solutions of strong acids [6], and hence, to infer estimated ranges of H_0 for specific sites. The implied correlation between indicator behaviour at the solid/gas interface and in aqueous solution has been criticised [7]. Furthermore, indicator colour changes may also be caused by adsorption at sites not involved in proton transfer equilibria [7–10]. A solution to the latter problem would be to use IR spec-

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troscopy to unambiguously characterise modes of adsorption of weak bases on oxidic surfaces.

Substituted acetophenones have been used as indicators in concentrated aqueous acids [11] and with pK_{BH}^+ values in the range -4.73 to -7.94 are potentially useful for identifying Brønsted acidic sites on silica–aluminas. Uman-sky and Hall [10] concluded that $-8.7 < H_0 < -3.3$ for two silica–alumina catalysts, although others have suggested much higher acidities [12–14]. UV–visible spectra of adsorbed benzalacetophenone have shown the existence of both protonated and neutral molecules [9,10], the former being dominant at low surface coverages [10]. One conclusion was that benzalacetophenone was unsatisfactory as an indicator of Brønsted acid sites [9]. We now report infrared spectra of acetophenone and 4-methoxyacetophenone on silica–alumina recorded in order to test whether adsorption on Lewis and

Brønsted acidic sites could be distinguished, and hence, ranges of H_0 of Brønsted acidic sites determined. Benzalacetophenone was too involatile to be adsorbed from the gas phase.

2. Experimental

Self-supported discs of silica–alumina (Aldrich, grade 135; 13% alumina; pore volume $0.77 \text{ cm}^3 \text{ g}^{-1}$; surface area $477 \text{ m}^2 \text{ g}^{-1}$) mounted in an infrared cell were heated in an air flow ($100 \text{ cm}^3 \text{ min}^{-1}$, 1 h) followed by vacuum (17 h) at 773, 373 or 473 K before cooling to ambient temperature (ca. 295 K), and exposure to adsorbate vapour which was progressively added in small aliquots. Spectra were recorded at 4 cm^{-1} resolution with a Perkin-Elmer 1720 FTIR spectrometer.

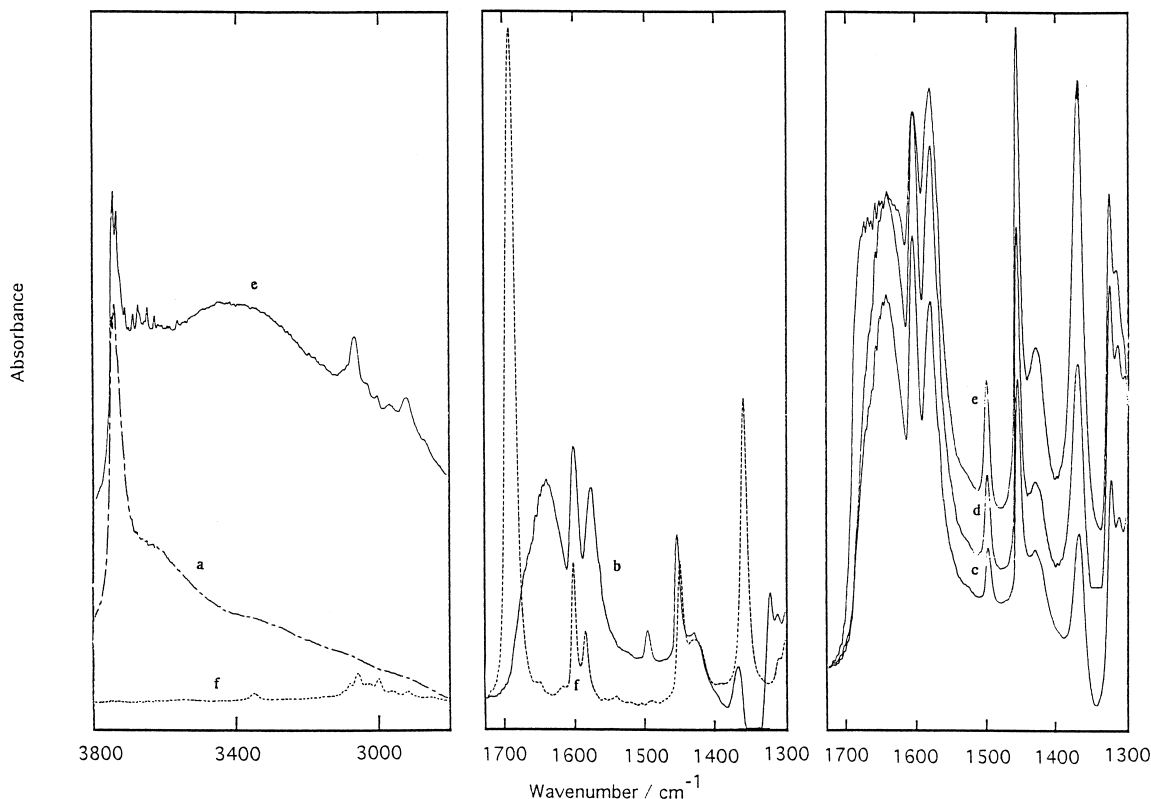


Fig. 1. Spectra of (a) silica–alumina (773 K), (b)–(e) with increasing adsorption of acetophenone and (f) liquid acetophenone.

3. Results

3.1. Adsorption of acetophenone

The spectrum of liquid acetophenone contained maxima at 1685 ($\nu(\text{CO})$), 1598, 1583, 1494, 1448 (aromatic ring vibrations), 1428 ($\delta_{\text{as}}(\text{CH}_3)$) and 1358 cm^{-1} ($\delta_{\text{s}}(\text{CH}_3)$). Comparison with spectra for acetophenone adsorbed on silica–alumina (773 K) showed that the biggest band shifts were for the $\nu(\text{CO})$ vibration that moved to 1635 cm^{-1} with a weak shoulder at ca. 1670 cm^{-1} , the 1358 cm^{-1} band that moved to 1364 cm^{-1} , and the band at 1583 cm^{-1} that moved to 1574 cm^{-1} (Fig. 1). These shifts are consistent with ligation of acetophenone via the carbonyl O-atom to Lewis acidic surface sites [15]. The band at 1494 cm^{-1} was vw for liquid acetophenone (Fig. 1f), but was stronger relative to other bands for acetophenone on silica–

alumina. The band was weak for acetophenone involved in hydrogen bonding interactions with silanol groups on silica but was much stronger, as for silica–alumina, for acetophenone ligated to Lewis acidic sites on titania. The present band is therefore ascribed to acetophenone ligated to Lewis acidic Al^{3+} sites. Further evidence for the perturbation of methyl groups in ligated acetophenone was also shown by weakening of a band at 3000 cm^{-1} assigned to a $\nu(\text{CH}_3)$ vibration [15]. The shoulder at 1670 cm^{-1} became relatively stronger at higher surface coverages and, in accordance with evidence from the OH-stretching spectral region may be ascribed to carbonyl groups involved in hydrogen bonding interactions with surface hydroxy groups. Perturbed hydroxy groups gave a broad band at 3400 cm^{-1} . Adsorption was accompanied by the growth of a narrow band at 1324 cm^{-1} (Fig. 1), which was absent from

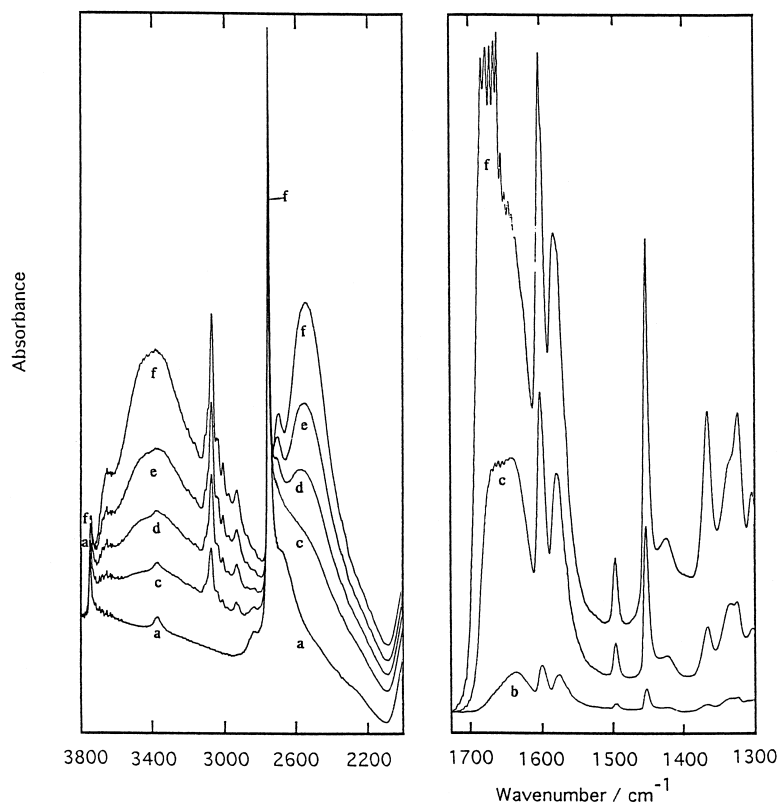


Fig. 2. Spectra of (a) deuterated silica–alumina (473 K), (b)–(f) with increasing adsorption of acetophenone.

spectra of liquid acetophenone. The initially white disc turned yellow in the presence of acetophenone.

Adsorption of acetophenone on silica–alumina (373 K) gave similar bands to those in Fig. 1. However, at low coverages, a maximum at 1662 cm^{-1} now dominated the $\nu(\text{CO})$ region, suggesting that hydrogen bonding to water molecules at Lewis acidic sites or to surface hydroxy groups was the main initial mode of adsorption. At higher coverage, ligation occurred and the band at 1662 cm^{-1} , which initially had a weak shoulder at 1635 cm^{-1} , became a composite band envelope with the maximum tending towards 1635 cm^{-1} at high coverages. The band at 1324 cm^{-1} was present but weak compared with the result for silica–alumina (773 K). The disc turned pale yellow during adsorption.

Acetone on oxide [16,17] or zeolite [18] surfaces can form enolate complexes [16,17], which

may condense with a further acetone molecule to form mesityl oxide [16,18]. One test for enolisation is that H/D isotopic exchange should occur between CH_3 groups and OD groups on a deuterated oxide surface.

Repeated exposure of silica–alumina to deuterium oxide vapour at 473 K failed to completely exchange the hydroxy groups present (Fig. 2a) showing that some groups were inaccessible to adsorbate molecules. A residual band at 3745 cm^{-1} due to silanol groups was accompanied by a weak band at 3382 cm^{-1} . A similar band to the latter at 3410 cm^{-1} for rutile was ascribed to bridging hydroxy groups [19] at sub-surface lattice sites [20,21]. Subsequent adsorption of acetophenone gave bands due to vibrations of adsorbed molecules similar to those for adsorption on the protiated surface including a prominent band at 1324 cm^{-1} (Fig. 2b–f). Apparent fine structure at the $\nu(\text{CO})$ band maximum at high coverage was due to apodisation

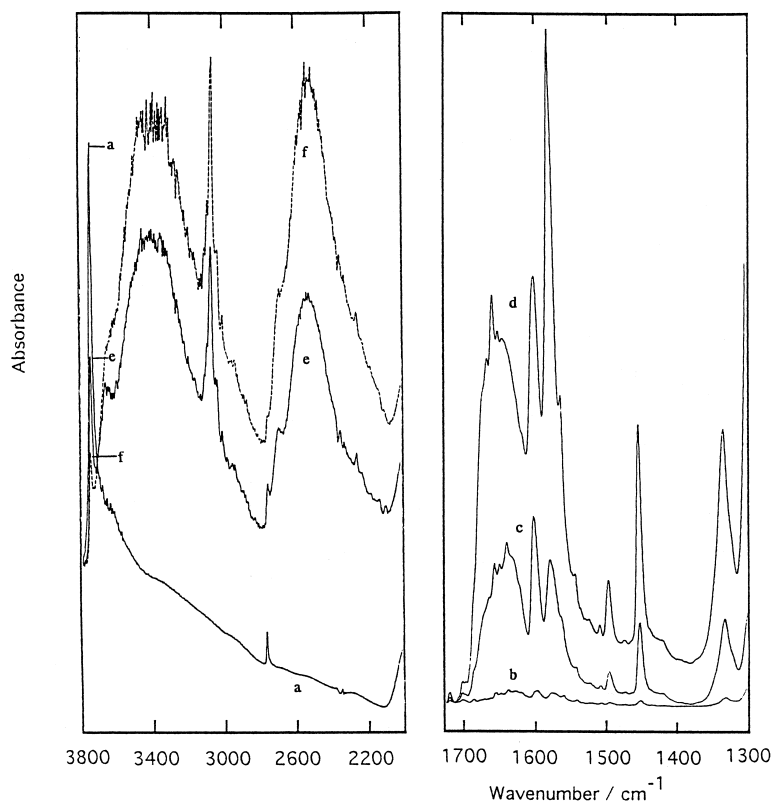


Fig. 3. Spectra of (a) slightly deuterated silica–alumina (773 K), (b)–(f) with increasing adsorption of acetophenone-methyl- d_3 .

failure for a high-intensity band. Spectra in the OD-stretching region showed that terminal SiOD groups giving the sharp maximum at 2757 cm^{-1} were perturbed by deuterium bonding to carbonyl groups giving a broader maximum at 2553 cm^{-1} . The growth of a distinct maximum at 2701 cm^{-1} further suggested that OD groups were also deuterium-bonded to aromatic ring π -electrons in adsorbed molecules [22]. The parallel growth of bands at 3400 and 3652 cm^{-1} due to hydroxy groups perturbed by hydrogen bonding with carbonyl groups and aromatic nuclei occurred without loss of intensity of the band at 3745 cm^{-1} due to residual hydroxy groups. This implies that hydroxy groups were being generated by H/D exchange involving OD and CH_3 groups. The proportion of adsorbed acetophenone molecules that had undergone exchange must have been small because no significant changes in the $\nu(\text{CH})$ or $\delta(\text{CH})$

spectra could be detected, nor was there a detectable band due to $\nu(\text{CD})$ vibrations. The only hint of deuterium in adsorbed molecules was a shoulder at 1337 cm^{-1} (Fig. 2), absent for acetophenone on an OH surface (Fig. 1), but strong for acetophenone-methyl- d_3 on both OH (Fig. 3) and OD (Fig. 4) surfaces.

3.2. Adsorption of acetophenone-methyl- d_3

The H/D exchange result was confirmed by adsorbing the CD_3 compound onto protiated silica-alumina that had been very slightly deuterated (Fig. 3). Spectra in the $1750\text{--}1300\text{ cm}^{-1}$ region were similar to those for acetophenone, except that bands due to $\delta(\text{CH}_3)$ vibrations were absent. The experiment was continued to high surface coverages when the sharp band at 3745 cm^{-1} had been largely replaced by the bands at 3652 and 3400 cm^{-1} due to

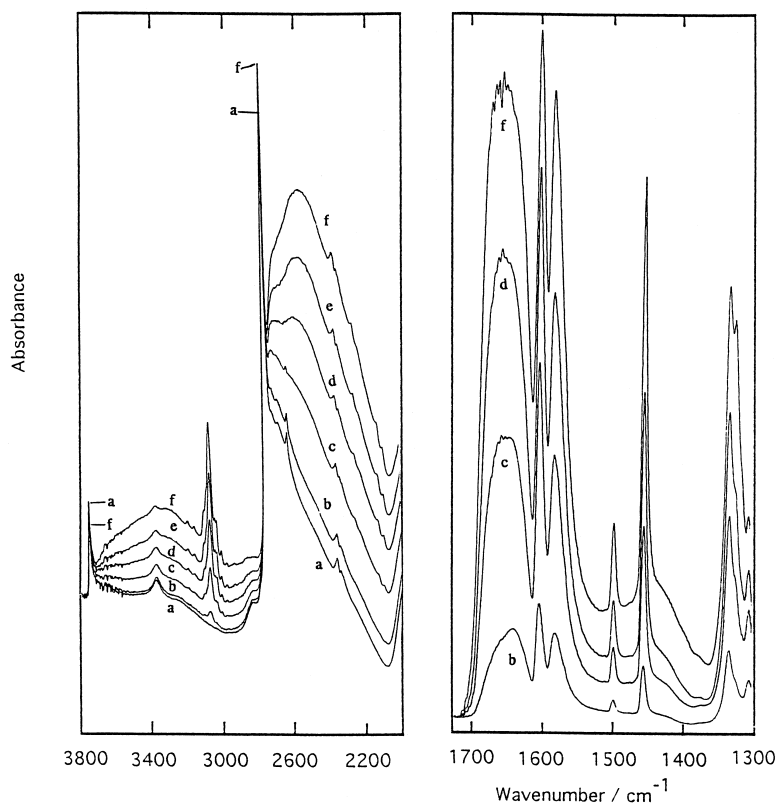


Fig. 4. Spectra of (a) deuterated silica-alumina (473 K), (b)–(f) with increasing adsorption of acetophenone-methyl- d_3 .

H-bonded OH groups. However, strong bands due to similarly D-bonded OD groups also grew at 2701 and 2553 cm^{-1} . The deuterium atoms can only have come from the CD_3 in adsorbed molecules, and therefore, this precludes the slight possibility that the results in Fig. 2 for an experiment lasting over 24 h might have been due to the ingress of atmospheric water vapour to the infrared cell. The overall growth of intensity of bands due to perturbed OH/OD groups was slightly larger than expected compared with the initial intensity of the band at 3745 cm^{-1} , suggesting that not only exchange but also the generation of further OD groups may have occurred. Results for acetophenone-methyl- d_3 on deuterated silica–alumina (473 K) supported this conclusion. Some unexchanged accessible OH groups remained and were perturbed by hydrogen bonding. However, the appearance of dominant bands due to perturbed OD groups was

also accompanied by a slight apparent increase in band intensity at 2757 cm^{-1} (Fig. 4). This was probably due to a change of slope of the spectral baseline as adsorption took place, although the fact remains that an increase in band intensity at 2553 cm^{-1} was accompanied by a relatively smaller change at 2757 cm^{-1} .

For acetophenone-methyl- d_3 on silica–alumina (373 K), the $\nu(\text{CO})$ region was dominated by the band at 1670 cm^{-1} due to H-bonded species with a comparatively weak shoulder at ca. 1635 cm^{-1} due to ligated species. The OH/OD region gave poor spectra.

3.3. Adsorption of 4-methoxyacetophenone

Only low surface coverages could be studied for this involatile solid. A $\nu(\text{CO})$ band at 1662 cm^{-1} was accompanied by evidence for a weak broad band at ca. 3365 cm^{-1} , these effects

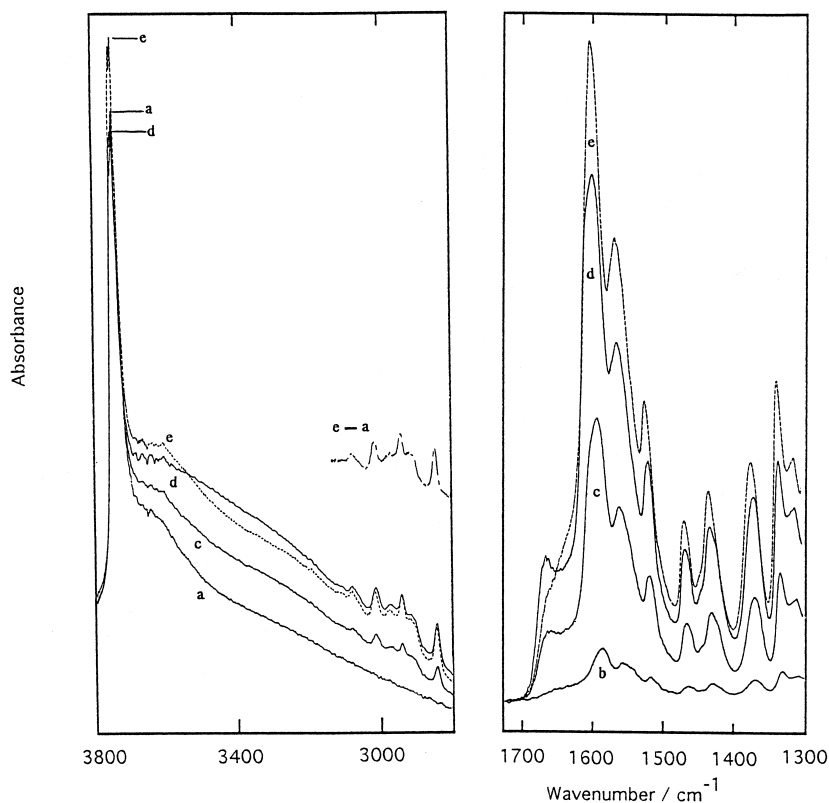


Fig. 5. Spectra of (a) silica–alumina (773 K), (b)–(e) with increasing adsorption of 4-methoxyacetophenone.

being attributable to hydrogen bonding interactions. However, with increasing time these bands were weakened, the former being replaced by a shoulder at ca. 1635 cm^{-1} due to ligated carbonyl groups (Fig. 5). Shifts of bands due to other vibrations of adsorbed molecules appeared to be much greater for 4-methoxyacetophenone than for acetophenone. Bands for the solid at $1604, 1576, 1509, 1418$ and 1359 cm^{-1} were at $1603, 1575, 1514, 1420$ and 1365 cm^{-1} for the 4-OMe compound on silica, but were at $1586, 1554, 1516, 1431$ and 1374 cm^{-1} for silica–alumina. The magnitude of the shifts, particularly for the bands at 1604 and 1576 cm^{-1} due to aromatic ring vibrations, were much greater than those reported for acetophenone ligated to metal cations in inorganic complexes [15].

A strong band at 1334 cm^{-1} (Fig. 5) was absent for solid 4-methoxyacetophenone or the compound adsorbed on silica. Although the relevant spectral region was noisy, there was also evidence for a weak sharp band at 3605 cm^{-1} . The disc turned dark yellow as adsorption proceeded.

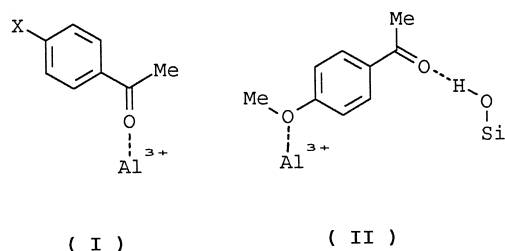
3.4. Adsorption of pyridine

Pyridine on silica–alumina (773 K) gave a spectrum closely similar to that of Basila et al. [2], except that the band at 1545 cm^{-1} due to protonated pyridine was weaker here compared with the band at 1450 cm^{-1} due to pyridine ligated to Lewis acidic sites. Here, the Brønsted site:Lewis site ratio [2] was ca. 0.35:1. For silica–alumina (373 K) the ratio became ca. 2.1:1 because the presence of adsorbed water enhanced the number of Brønsted sites at the expense of Lewis sites on the surface [2].

4. Discussion

The surface of silica–alumina contains Lewis acidic sites of different strengths corresponding to coordinatively unsaturated Al^{3+} ions in octahedral and tetrahedral (two types) configura-

tions [23,24]. The ligation of the acetophenones according to structure I failed to distinguish the different sites.

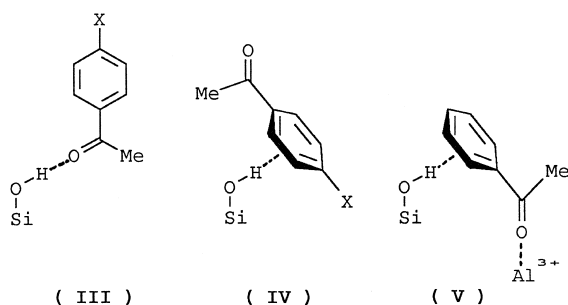


Parallel experiments involving acetone adsorption on silica–alumina (773 K) at low coverages also only gave a single band at 1680 cm^{-1} due to $\nu(\text{CO})$ for ligated species. The OH spectral region gave no evidence for hydrogen bonding, confirming that the strongest mode of adsorption of the ketones involved ligation to Al^{3+} sites. The $\nu(\text{CO})$ band positions for the acetophenones in solution in CCl_4 are, in terms of 4-substituent, 1684 (OMe) and 1692 cm^{-1} (H), the difference reflecting the electronic effect of the OMe substituent [25,26]. The band positions were the same (1635 cm^{-1}) for the two ketones ligated to the silica–alumina surface.

The absence of a $\nu(\text{CO})$ band due to free carbonyl groups for the adsorbed OMe compound shows that the molecule was not adsorbed via ligation involving OMe groups with the carbonyl groups remaining unperturbed. However, ether [27] groups may ligate to Lewis acidic surface sites. The spectra of adsorbed 4-methoxyacetophenone initially showed, unlike the result for acetophenone, a dominant $\nu(\text{CO})$ band due to hydrogen bonded species. Ligation via the methoxy group but with simultaneous hydrogen bonding of the carbonyl group with a surface silanol group would account for this result that is represented by II.

Spectra in the OH/OD regions for acetophenone resemble results for the adsorption of substituted anisoles on silica at the solid/liquid interface [22]. Here, hydrogen bonding involv-

ing both aromatic π -electrons and carbonyl groups occurred the latter giving the bigger $\Delta\nu(\text{OH})$ spectroscopic shift. The strong growth of a $\nu(\text{CO})$ band (Fig. 2) due to hydrogen bonded species at high coverages, and the dominance of the same $\nu(\text{CO})$ band for silica–alumina (373 K) at low coverages show that some molecules were adsorbed solely through hydrogen bonding interactions involving surface silanol groups and carbonyl groups as in III.



The relative intensities of the bands at 3400 and 3652 cm^{-1} (Fig. 2) were of similar magnitude to the results for anisoles [22], suggesting, in accordance with the previous conclusions, that structure (IV) represents a competing, but much weaker mode of adsorption than III. A further possibility is that ligated acetophenone adjacent to surface silanol groups could simultaneously interact with the latter via hydrogen bonding in accordance with V. However, the parallel growth of the bands at 3400 and 3652 cm^{-1} suggest that IV rather than V was the dominant species responsible for the latter band.

A mechanism involving enolisation, which may be acid or base catalysed [28], would account for the results of the H/D exchange experiments. Enolisation of acetone is base catalysed on rutile [16] but acid catalysed in H-ZSM-5 [18]. The spectroscopic recognition of adsorbed enolate for acetone on rutile was not achieved for acetophenone on silica–alumina, showing that the enolate anion formed in a base-catalysed mechanism [16] could, at most, only have been a transitory intermediate on

silica–alumina. Evidence for protonated acetophenone that would be formed in an acid-catalysed mechanism was equivocal, although this mechanism may be deemed more likely on silica–alumina.

Condensation reactions of acetone to mesityl oxide have been shown to follow both base catalysed enolisation over rutile [16] and acid catalysed enolisation over H-ZSM-5 [18]. In accordance with a similar unpublished result for 4-methylacetophenone on the present silica–alumina, the spectrum in Fig. 5e was recorded after 16 h contact between oxide and adsorbate and showed a time-dependent effect involving the removal of hydrogen bonded adsorbate and the growth of a $\nu(\text{CO})$ band due to ligated adsorbate. However, the condensation reaction, which would give dypnone $\text{Ph}(\text{Me})\text{C}=\text{CHCOPh}$ from acetophenone, leads to water, which should appear in tact or as OH groups on the oxide surface. Slight growth of the band at 3745 cm^{-1} occurred (Fig. 5i and 6e), but must have arisen because of the partial loss of $\text{SiOH}-\text{O}=\text{C}$ interactions. Some evidence for new hydroxy groups derived from water (or D_2O) came from the spectra in Figs. 2–4, although the dominant effects in the OH/OD spectral region involved the formation of hydrogen bonded complexes and H/D exchange reactions. Condensation reactions only occurred to a minor extent on silica–alumina at 295 K.

Ab initio Hartree–Fock calculations at the SCF level (3–21 G basis set) have been carried out for acetophenone and for acetophenone protonated on the carbonyl O-atom. After appropriate scaling, the two highest frequency aromatic ring vibrations were predicted to be at 1606/1584 cm^{-1} for PhCOMe and 1587/1559 cm^{-1} for PhCOHMe^+ . For acetophenone and 4-methoxyacetophenone on silica the bands were at 1601/1584 and 1603/1578 cm^{-1} showing a closeness of band positions for the two compounds, neither of which were protonated. The dominant bands for acetophenone on silica–alumina were at 1598/1574 cm^{-1} again, suggesting that protonation had not occurred. In

contrast, for 4-methoxyacetophenone on silica–alumina bands at 1586/1554 cm^{-1} exhibited significant shifts possibly as a result of protonation. Comparison of other bands in the spectra with the predictions concurred with this conclusion.

Benzalacetophenone ($\text{p}K_{\text{BH}}^+ = -5.60$) was adsorbed in the protonated form on silica–aluminas at low coverages, but in the neutral form at higher coverages [9,10]. The present results show that the latter must have involved ligation to Lewis acidic Al^{3+} sites and hydrogen bonding with surface silanol groups. Acetophenone is a weaker base with $\text{p}K_{\text{BH}}^+ = -6.15$ [11], and is therefore less likely to be protonated unless H_0 for acidic hydroxy groups is approaching this value. No evidence for protonation appeared in the IR spectra, although the bands could have been obscured by more intense maxima due to neutral species. There was some evidence of protonation from the spectroscopic shifts for the 4-MeO compound for which $\text{p}K_{\text{BH}}^+ = -4.81$ [11]. That the stronger base is the most likely to be protonated is logical. However, unfortunately, an alternative explanation of the band shifts would be that the electron donating property of the methoxy group [29] favours enhanced quinonoid character [26] of the molecule ligated to Lewis acidic sites. This would cause a red shift in the electronic spectrum, and may confuse the use of this indicator colourimetrically unless, as before [9,10], UV–visible spectra are recorded in detail. Protonated 4-methoxyacetophenone would also have significant quinonoid character [11].

The ab initio calculations predict a band at 1317 cm^{-1} due to the $\nu(\text{CO})$ vibration of protonated acetophenone. Spectra of acetophenone on silica–alumina showed a band at 1324 cm^{-1} , which was not present for the compound adsorbed on silica. However, if this band was due to protonated acetophenone, then the band at 1324 cm^{-1} should have been absent for acetophenone on a deuterated surface. This was not the case (Fig. 2), although the obvious implication that protonation had not therefore occurred

was impaired by the generation of surface hydroxy groups via the exchange reaction between OD groups and CH_3 groups. The adsorption of acetophenone-methyl- d_3 on a deuterated surface (Fig. 4) did not help because the spectrum of the neutral adsorbate contained two bands at 1310–1320 cm^{-1} , which would be shifted upwards on ligation of acetophenone to Lewis acidic sites [15]. On balance, therefore, the ab initio calculations combined with the infrared results suggest that acetophenone was not protonated on silica–alumina.

The colour changes for the present samples were to dark yellow for the OMe compound and to pale yellow for acetophenone. Umansky et al. [30] deduced for two silica–aluminas that the strongest acid sites had H_0 values of -5.6 and -5.8 . These values are consistent with the observed protonation of benzalacetophenone [9,10]. The $\text{p}K_{\text{BH}}^+$ value of acetophenone (-6.15) is therefore close to the H_0 values, and the colour change for the indicator could indicate that protonation had occurred, although there was no infrared evidence for protonation with the possible exception of the band at 1324 cm^{-1} . For the strong base 4-methoxyacetophenone (-4.81), the infrared evidence was more substantial, and protonation probably took place.

The apparent absence of protonation for acetophenone is consistent with results for the adsorption of acetone on zeolites [31–35]. Acetone is a stronger base than acetophenone and zeolites are, in general, more Brønsted-acidic than silica–aluminas. However, both infrared [31–33] and NMR data [34,35] suggest that hydroxy groups, including those which are Brønsted acidic, in zeolites predominantly form neutral hydrogen-bonded complexes with adsorbed acetone molecules. The present lack of evidence for protonation of acetophenone contributes to inconsistent conclusions drawn from infrared and NMR data on the one hand [31–35], and UV–visible spectroscopy on the other [10,12–14]. Values of $H_0 < -11$ deduced for silica–aluminas using nitroaromatic indicators

[12–14] are at fault because indicator colour changes must have occurred for reasons other than protonation [7,10]. The evidence from which it was deduced that $-8.7 < H_0 < -3$ for two silica–aluminas [10] is also suspect because of the choice of indicators for H_0 assessment. The use of benzalacetophenone has been criticised [9] because, as may be occurring here for 4-methoxyacetophenone, shifts in electronic spectra giving rise to colour may result from the electronic effects of indicator ligation to Lewis acidic sites. Both Ph_3COH ($pK_{\text{BH}}^+ = -3.3$) and 2,4,6-trimethylbenzyl alcohol ($pK_{\text{BH}}^+ = -8.7$) are J_0 (or H_{R}) indicators [36]. Their different behaviour from Hammett bases in solution results from differences in solvation, and hence activity coefficient behaviour. Translation of data for J_0 indicators into H_0 values relating to behaviour at the solid–gas interface must be questionable. Furthermore, the carbonium ions resulting from indicator ionisation may not necessarily be formed via a mechanism involving protonation and loss of water [36], but could also be generated via the adsorption of the indicators on Lewis acidic sites [8]. Thus, for example, the adsorption of Ph_3COH on anatase to give Ph_3C^+ ions [37] must involve Lewis acidic sites [8], as anatase is not Brønsted acidic.

5. Conclusion

It appears that the use of visible indicators to establish H_0 acidity values at the solid/gas interface is open to question unless it can be unambiguously proved that indicator protonation is the sole cause of spectroscopic change. Irreversible surface reactions or adsorption behaviour at sites other than Brønsted acidic hydroxy groups may lead to spectroscopic changes that are wrongly interpreted. Infrared spectroscopy provides a better opportunity, as with pyridine adsorption [4], to test the existence of protonation, although van Santen and Kramer [31] pointed out that erroneous interpretations of spectra of acetone, methanol and water on zeo-

lites have been published. Limitations of the H_0 scale applied to solid surfaces have been expressed and the use of ^{13}C NMR spectroscopy propounded as a good method for acidity determination [38,39].

Acknowledgements

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References

- [1] M.R. Basila, T.R. Kantner, *J. Phys. Chem.* 71 (1967) 467.
- [2] M.R. Basila, T.R. Kantner, K.H. Rhee, *J. Phys. Chem.* 68 (1964) 3197.
- [3] J.W. Ward, R.C. Hansford, *J. Catal.* 13 (1969) 154.
- [4] E.P. Parry, *J. Catal.* 2 (1963) 371.
- [5] J.J. Christensen, L.D. Hansen, R.M. Izatt, *Handbook of Proton Ionization Heats and Related Thermodynamic Quantities*, Wiley-Interscience, New York, 1976, p. 168.
- [6] C.H. Rochester, *Acidity Functions*, Chap. 1, Academic Press, London, 1970.
- [7] I. Ahmad, T.J. Dines, C.H. Rochester, J.A. Anderson, *J. Chem. Soc., Faraday Trans.* 92 (1996) 3225.
- [8] C.H. Rochester, *Discuss. Faraday Soc.* 52 (1971) 285.
- [9] H.V. Drushel, A.L. Summers, *Anal. Chem.* 38 (1966) 1723.
- [10] B.S. Umansky, W.K. Hall, *J. Catal.* 124 (1990) 97.
- [11] R. Stewart, K. Yates, *J. Am. Chem. Soc.* 80 (1958) 6355.
- [12] M. Hino, S. Kobayashi, K. Arata, *J. Am. Chem. Soc.* 101 (1979) 6440.
- [13] H. Hattori, T. Osamu, M. Ta Agi, K. Tanabe, *J. Catal.* 68 (1981) 132.
- [14] K. Hashimoto, T. Matsuda, H. Motoyama, H. Yakushiji, M. Ono, *Ind. Eng. Chem. Prod. Res. Dev.* 25 (1986) 243.
- [15] W.L. Driessen, W.L. Groeneveld, *Rec. Trav. Chim.* 111 (1971) 258.
- [16] D.M. Griffiths, C.H. Rochester, *J. Chem. Soc., Faraday Trans.* 74 (1978) 403.
- [17] H. Miyata, Y. Toda, Y. Kubokawa, *J. Catal.* 32 (1974) 155.
- [18] A.I. Biaglow, J. Sepa, R.J. Gorte, D. White, *J. Catal.* 151 (1995) 373.
- [19] D.M. Griffiths, C.H. Rochester, *J. Chem. Soc., Faraday Trans.* 73 (1977) 1510.
- [20] A.D. Buckland, C.H. Rochester, D.-A. Trebilco, K. Wigfield, *J. Chem. Soc., Faraday Trans.* 74 (1978) 2393.
- [21] J. Graham, C.H. Rochester, R. Rudham, *J. Chem. Soc., Faraday Trans.* 77 (1981) 2735.
- [22] C.H. Rochester, D.-A. Trebilco, *J. Chem. Soc., Faraday Trans.* 74 (1978) 1125.
- [23] A. Leonard, S. Surzuki, J.J. Fripiat, C. De Kimpe, *J. Phys. Chem.* 68 (1964) 2608.

- [24] G. Connell, J.A. Dumesic, *J. Catal.* 102 (1986) 216.
- [25] N. Fuson, M.-L. Josien, E.M. Shelton, *J. Am. Chem. Soc.* 76 (1954) 2526.
- [26] R.N. Jones, W.F. Forbes, W.A. Mueller, *Can. J. Chem.* 35 (1957) 504.
- [27] J. Graham, R. Rudham, C.H. Rochester, *J. Chem. Soc., Faraday Trans.* 180 (1984) 895.
- [28] R.P. Bell, *The Proton in Chemistry*, Chap. 9, Chapman & Hall, London, 1973.
- [29] G.B. Barlin, D.D. Perrin, *Q. Rev.* 20 (1966) 75.
- [30] B. Umansky, J. Engelhardt, W.K. Hall, *J. Catal.* 127 (1991) 128.
- [31] R.A. van Santen, G.J. Kramer, *Chem. Rev.* 95 (1995) 637.
- [32] A. Zecchina, S. Bordiga, G. Spoto, D. Scarano, G. Spanò, F. Geobaldo, *J. Chem. Soc., Faraday Trans.* 92 (1996) 4863.
- [33] J. Florián, L. Kubelkova, *J. Phys. Chem.* 98 (1994) 8734.
- [34] A.I. Biaglow, R.J. Gorte, G.T. Kokotailo, D. White, *J. Catal.* 148 (1994) 779.
- [35] A.I. Biaglow, J. Sepa, R.J. Gorte, D. White, *J. Catal.* 151 (1995) 373.
- [36] C.H. Rochester, *Acidity Functions*, Chap. 3, Academic Press, London, 1970.
- [37] H.P. Boehm, *Discuss. Faraday Soc.* 52 (1971) 264.
- [38] D. Farcasiu, A. Ghenciu, G.J. Miller, *J. Catal.* 134 (1992) 188.
- [39] D. Farcasiu, A. Ghenciu, *J. Catal.* 134 (1992) 126.